Charge transfer in molecular conductors — oxidation or reduction?

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We discuss the nature of charge transfer in molecular conductors upon connecting to two metallic contacts and imposing a voltage bias across them. The sign of the charge transfer (oxidation vs. reduction) depends on the position of the metal Fermi energy with respect to the molecular levels. In addition, the charge transfer depends on the strength of the coupling (chemisorption vs. physisorption) with the contacts. A convenient way to establish the nature and onset of the charge transfer and the corresponding features in the I-V is to draw an energy level diagram for each spin species. Starting from such a level diagram, we argue that transport in the Tour-Reed switching molecules, which consist of a central phenyl ring with a nitroamine redox center, involves the oxidation of a highest occupied molecular orbital (HOMO)-based level.

In recent years, there have been many reports of conductance characteristics measured for individual molecules or small ensembles of oriented molecules [1]. Understanding transport in molecular conductors is quite challenging because of its special status between solid state physics and molecular chemistry. On the one hand, the system differs from conventional solid-state devices where conduction is understood in terms of alignment of a band structure that is largely unaffected by charge transfer or the nature of the contacts. On the other hand, in contrast to conventional chemistry, the molecule is not an isolated unit in equilibrium; coupling with metallic contacts makes the system an open one, capable of freely exchanging a fractional amount of charge to and from the contacts. In addition in the presence of a voltage bias across the molecule, the system is out of equilibrium and equilibrium statistical mechanical techniques become inapplicable. Predicting I-V characteristics of molecular conductors involves therefore a suitable combination of techniques and insights both from chemistry as well as from mesoscopic physics.

We have recently developed a self-consistent, ab-initio procedure for calculating I-V characteristics of molecular conductors [2]. In this procedure, we self-consistently combine the outputs of a standard quantum chemical software (GAUSSIAN98) with a non-equilibrium Green's function (NEGF) formalism for transport in an open, voltage-biased system. The method takes into account the hybridization of molecular levels with the contacts exactly, and can be used both for weak and strong contacts. In this paper, we will focus on an intuitive picture that can be used to gain qualitative insight into the nature of conduction through a molecule. This picture is particularly useful when the contacts are weakly coupled, and issues related to level broadening are minor. The first step is to obtain the energy levels of an isolated molecule

and locate the Fermi energy E_F of the metallic contacts, as shown in Fig. 1 (a). Under bias the electrochemical potentials $\mu_{1,2}$ of the contacts separate as shown in Fig. 1(b). We wish to address the following questions in this paper: (a) which molecular levels are involved in the conduction process? (b) Does the molecule get oxidized ($M \to M^+$) or reduced ($M \to M^-$) at steady state?

Equilibrium energy level diagram ($V = 0$). We start by obtaining an equilibrium energy level diagram as in Fig. 1(a). The energy levels for a given molecule are obtained using a standard quantum chemical software like Hyperchem, MOPAC or GAUSSIAN98. The equilibrium Fermi energy of gold is known to be $E_F = -5.1$ eV. It is important to note that semi-empirical programs like Extended Hückel Theory do not give the correct absolute value for molecular energy levels. In that case, the energy levels for gold must also be computed using the same program for consistency [3].

Which levels conduct?. Fig. 1 shows a schematic description of transport through a mesoscopic device. At equilibrium (Fig. 1(a)) the metal contacts impose their common electrochemical potential on the molecule, equal to the metal fermi energy E_F. Coupling of the molecule with the contacts broadens each highest occupied (HOMO)/lowest unoccupied (LUMO) molecular orbital-based level, so that the number of electrons below the fermi energy is now fractional (the deviation of this number from the number of electrons for the isolated molecule is a measure of charge transfer between the molecule and the contacts at equilibrium). When a voltage bias is imposed (Fig. 1(b)), the system is driven out of equilibrium and the contact potential splits: $\mu_{1,2} = E_F \mp eV/2$. (Note that in contrast to our earlier convention of fixing energy levels and varying the contact potentials with bias by different amounts depending on the ratio of couplings [4,5], we now vary the electrochem-

ical potentials as above and let the energy levels adjust accordingly). For adiabatic, reflectionless contacts and ballistic transport, the contact potentials are imposed separately on the right and left-moving electrons [6]. As long as the two electrochemical potentials lie in the gap, all HOMO levels lie below both potentials and are filled at zero temperature, the LUMO levels lie above the potentials and are empty, and there is no current. When the bias is sufficient that a level is crossed by one of the electrochemical potentials, that level is emptied out (oxidized) from one side but filled (reduced) from the other, with a resultant onset of current. Thus only levels which lie between the two electrochemical potentials contribute to conduction at zero temperature (at finite temperature, this range is extended by the thermal energy $\pm k_B T$). The onset of current is determined by the proximity of the Fermi energy to the molecular level closest to it.

Oxidized or reduced?. The coupling to the contacts of an extended molecule is described by a non-hermitian self-energy matrix Σ calculated in an appropriately chosen basis [6]. This self-energy effectively partitions the problem into the molecular part and the contact, and leads to a conceptual simplification of the problem. The broadenings of the levels (inverse lifetime) are described by the anti-hermitian components $\Gamma_{1,2}$ of $\Sigma_{1,2}$. For fermi functions $f_{1,2}$ corresponding to the two contact potentials $\mu_{1,2}$, the steady-state occupancy of a molecular level is given by $f = (f_1 \Gamma_1 + f_2 \Gamma_2)/(\Gamma_1 + \Gamma_2)$. If the level lies between $\mu_{1,2}$ at zero temperature, $f_1 = 0$ and $f_2 = 1$ so that the occupancy is given by $f = \Gamma_2/(\Gamma_1 + \Gamma_2)$. One of the contacts is trying to add electrons (reduce), while the other is trying to remove them (oxidize). If the left contact is stronger than the right contact ($\Gamma_1 \gg \Gamma_2$), the level is emptied (oxidized) while in the opposite case the level stays filled (reduced). In either case, a current flows due to the competition between oxidation and reduction. Typically for a self-assembled monolayer, one end of the molecule (usually consisting of a thiol group chemisorbed on a gold surface) has a strong contact, while the other end is physisorbed and has a weak contact. This means that for a positive bias on the physisorbed end, the molecule remains neutral, while for opposite bias, charging occurs from the strongly contacted chemisorbed end [7].

For a high work function metal, E_F usually lies near the HOMO level. This is an issue that clearly needs a lot more attention, since the precise location of E_F depends on the model for the contacts, as well as the method of calculating the molecular Hamiltonian. A third terminal (gate) [8] can help resolve some of these issues. One of the consequences of a self-consistent evaluation of energy levels is that as we raise the fermi energy, the levels float up by an amount equal to the charging energy (for a solid, this is roughly given by the capacitance of a sphere of radius equal to the size of the electronic wave function). For a molecule with strong coupling to at least one contact, or for a molecule in solution, the effective electronic size is infinite, so that the charging energy is small, and classical STM theory holds. For a weakly coupled system, charging effects lead to the levels following the Fermi energy, so that the conduction tends to remain HOMO-based. We verified this for the phenyl-dithiol molecule (PDT) where we couple the outputs of a GAUSSIAN98 [9] evaluation of energy levels using a Becke-3 parameter exchange and Perdew-Wang 91 correlation (B3PW91) approximation [10,11], with a non-equilibrium Green's function (NEGF) evaluation of the density matrix [4,5], and iterate to convergence self-consistently [2]. The basis set used was the Los Alamos National Lab set for effective core potentials of the double ζ type (LANL2DZ) [12,13]. The converged energy levels increase with increasing E_F at the rate of 4eV/Volt, which corresponds to the capacitative charging energy of a sphere of size $5\mathring{A}$.

Level diagram under bias ($V \neq 0$). As an illustrative example, we have plotted the energy levels of the Tour-Reed molecule 2'-amino- 4,4'-di[ethynyl]phenyl-5'-nitro-1-[thioacetyl]benzene containing the nitroamine redox center [14], as a function of voltage applied to the sulphur end (Fig. 2). We consider an extended molecule including three surface gold atoms bonded to sulphur and obtain energy levels analogous to Fig. 1, including the effect of voltage-induced Stark shifts of the molecular orbitals. Exchange and correlation effects are included by performing a B3PW91 calculation with a LANL2DZ basis set using the GAUSSIAN 98 software. In the Tour-Reed experiment, one end of the molecule is self-assembled onto gold using sulphur "alligator clips", leading to a strongly coupled chemisorbed contact, while the other end is a carbon atom weakly coupled to an evaporated gold contact. Charging occurs when the electrochemical potential μ_1 of the sulphur end (dotted line in Fig. 2) crosses a molecular level. From Fig. 2, we see that for positive bias on sulphur, we first cross a HOMO level by the stronger sulphur contact, which oxidizes the molecule (the first LUMO level is actually a nonconducting gold-based level, as we discuss below). For negative bias, the HOMO level is crossed by the weaker carbon contact, so the level stays filled and there is no charging. This means that the I-V should be strongly asymmetric, as is indeed observed. * The sulphur contact potential μ_1 crosses the HOMO level at around 2 V, whereupon

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*For a spatially symmetric molecule, such contact-induced charging asymmetries alone determine the asymmetry in the I-V [15]. However for spatially asymmetric molecules such as the Tour-Reed example here, the I-V asymmetry is much larger, and given predominantly by the unequal Stark shifting of the intrinsic molecular wavefunctions (the asymmetric Stark shifting is seen in Fig. 2).

the molecule is oxidized from M to M^+. This is important, since the precise nature of the charging process is an important question raised in the literature [16,17]. Although cyclic voltammetric curves seem to suggest reduction processes as being operative, one has to remember that in such measurements counterions are present in solution, and substantially compromise any charging effects that may dominate in solid state.

When M changes to M^+, we need a whole new set of energy levels (Fig. 2). Two changes happen: (i) since one electron of a particular spin is pulled out by the contact, the spin degeneracy is removed; (ii) secondly, the removal of one electron of given spin leads to charging effects which cause all the levels of M^+ obtained from GAUSSIAN98 to float down by about 2 volts. This is unphysical, because GAUSSIAN98 models an isolated molecule with image charges at infinite distance. In the presence of image charges on the contacts, the charging energy will be lower. We therefore raise the energy levels of M^+ so as to align the energy level of the semi-occupied molecular orbital (SOMO) with the HOMO of the neutral species (M). Such an alignment is motivated by our assumption that in the absence of correlations and molecular reorganization, the ionization potential of M equals the electron affinity of M^+. This assumption is a point that requires further work, and should come automatically out of a proper ab-initio theory that includes the effect of image charges on the contacts. Note that in order to obtain spin-dependent charging effects that shift all levels except the SOMO substantially, one needs to do a spin-unrestricted (UHF/LSDA) calculation that breaks the spin degeneracy of the energy levels.

It is interesting to note that for an extended molecule, there are some gold-based levels. These can be identified either from their wave functions that are localized strongly on gold, or from their energy levels; the levels run roughly parallel to the electrochemical potential μ_1 of the contact on the chemisorbed side (dotted line in Fig. 2). For small molecules these gold levels, as well as metal-induced gap states (MIGS) that arise when a self-energy is included in our calculation, end up contributing to the conductance through direct tunneling processes. For large molecules such states hybridize with molecular wave functions, but don't contribute directly to tunneling, so they can be ignored. However the gold levels can still influence the positions of the other levels through level-repulsion, so the contacts affect the voltage at which a HOMO level is crossed and oxidation occurs.

We have shown that in self-assembled monolayers such as the Tour-Reed molecules containing the nitroamine redox center, charge transfer occurs due to oxidation from the strongly contacted end involving the level closest to the Fermi energy. We are currently investigating the mechanism of switching thereafter. Understanding the behavior of a molecular switch is important from the point of view of molecular electronics. Several switching

molecules have been reported [14,18], and various possible mechanisms suggested [17,19]. A charged species could deform in an applied field, and the electromechanical effect could switch off the current. If the added charge is localized on a sidechain of the molecule, it could rotate the central benzene ring attached to it in the presence of the field, distortiing the conjugated electron wave function enough to switch current off. A more complicated cooperative effect involving the whole self-assembled monolayer could also arguably lead to a current switch. Prior to a full self-consistent ab-initio calculation of transport properties including contact effects, it is important to develop an intuitive understanding of transport in the isolated species. An energy level diagram as illustrated above can serve as a quick intuitive tool to answer some basic questions such as the onset of current, whether an electron is being added or removed, or the existence of an asymmetry in the I-V.

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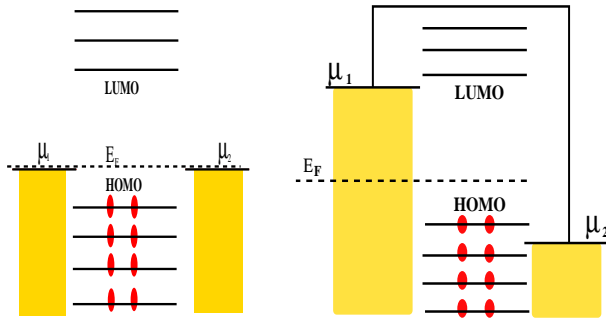[19] M. DiVentra, S.-G. Kim, S. T. Pantelides and N. D. Lang, Phys. Rev. Lett. **86**, 288 (2001).

FIG. 1. Simplified description of conduction in a mesoscopic device: (a) *Left:* At equilibrium (V = 0) the metal contact electrochemical potential is given by $\mu_{1,2} = E_F$. The molecular levels are discrete, but end up being broadened by coupling with contacts. (b) *Right:* Under bias (V> 0) the system is out of equilibrium as the contact potentials split, $\mu_{1,2} = E_F \mp eV/2$. Only the levels lying between μ_1 and μ_2 are filled from one side (oxidized) and emptied from the other (reduced) with a resultant conduction of current. Levels lying below or above both electrochemical potentials stay filled or empty and do not contribute to current at zero temperature.
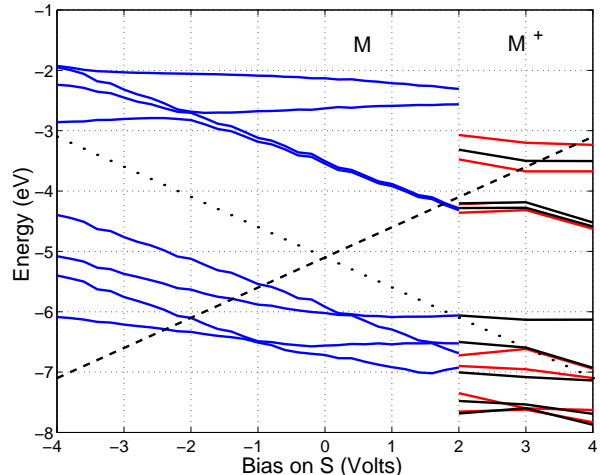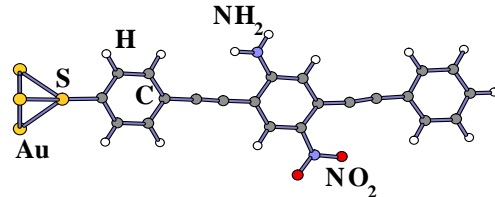

FIG. 2. *Top:* Tour-Reed molecule with nitroamine side-group, extended to include three gold atoms from the contact surface bonded directly to sulphur. The molecule has a strong chemisorbed bond at the sulphur side and a weak physisorbed one at the other. *Bottom:* Energy levels for the neutral molecule (M) as a function of voltage applied to the sulphur end. The levels Stark shift with applied voltage. There are some gold-based levels running roughly parallel to the electrochemical potential on sulphur μ_1 (dotted line), that do not contribute to conduction. The Fermi energy $E_F = -5.1$ eV is closer to the HOMO levels than the LUMO ones (ignoring the trivial gold-based levels). At positive bias, the HOMO level is crossed first with the strong sulphur contact (dotted line) around 2 V, which empties the level out (oxidation). Subsequently, we draw the energy levels for the oxidized species M^+, which are spin nondegenerate (red and black lines). At negative bias, the HOMO levels are crossed with the physisorbed carbon contact (dashed line), which does not charge up the system due to the weakness of the contact coupling. The resulting I-V is expected to be strongly asymmetric, and exhibits charging effects arising from an oxidation step at around 2 V.